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(71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW only): **UNILEVER PLC** [GB/GB];
Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NL, NO, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TR, UA, UZ, VN, YU only): **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **SHI, Yu-Shian**

[CN/CN]; Unilever Research, Shanghai Institute of Organic Chemistry, 354 Fenglin Road, Shanghai 200032 (CN). **SU, De-Bao** [CN/CN]; Unilever Research, Shanghai Institute of Organic Chemistry, 354 Fenglin Road, Shanghai 200032 (CN). **WU, Shang-Ren** [US/US]; Unilever Research U.S. Inc., 45 River Road, Edgewater, NJ 07020 (US).

(74) Agents: **FRANSELLA, Mary, Evelyn et al.**; Unilever PLC, Patent Dept., Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

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(54) Title: LAUNDRY COMPOSITION COMPRISING PERFLUOROALKYL SOIL RELEASE POLYMER

(57) Abstract: Polymeric material obtained by polymerising an ethylenically unsaturated perfluoroalkyl monomer and optionally other ethylenically unsaturated monomers, the polymer containing aromatic moieties can be used to give anti soil redeposition, soil release and oil repellency properties to fabric when used in the wash step or the rinse step of a laundry process.

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LAUNDRY COMPOSITION COMPRISING PERFLUOROALKYL SOIL RELEASE POLYMER

5

Introduction

The present invention relates to laundry compositions, in particular fabric wash compositions and laundry rinse conditioning compositions, comprising perfluoroalkyl soil release polymers. The present invention also relates to a method of treating fabric in a laundry process using perfluoroalkyl containing polymers.

15

Background and Prior Art

The use of soil release agents in laundry products is now well known. A number of classes of compounds have been used in the past.

Cellulose ether soil release polymers may be used, for example as described in GB 1534641. Polyester compositions are also well known as soil release polymers, for example as described in EP-A-0185427. The majority of soil release polymers used in practice belong to these two classes.

US 4043965 discloses copolymers of acrylic acid and 1,1-dihydroperfluoro-octyl methacrylate for applying a non-permanent soil release finish to fabric. The composition may be used for applying a soil release finish in the rinse cycle of a home laundry process.

30

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Specialised compositions for giving oil and water repellency to fabric are well known in the art of pre-treatment of fabric in the fabric manufacturing and clothes manufacturing industries. Perfluoroalkyl containing polymers and their use for giving oil and water repellency to fabrics in this way are known for example from EP-A-0195323, EP-A-0351513, EP-A-0424765, US 4550189 and US 5753569.

10 In these processes, the perfluoroalkyl containing polymers may be supplied as aqueous dispersions, dispersed using surfactants, for example as described in EP-A-0351513. In order to induce the compositions to adhere to the fabric, 15 the compositions may be relatively concentrated, as in EP-A-0424765. Alternatively, a resin may be used to fix the polymer onto the fabric as in EP-A-0195323.

Fabric laundry processes are fundamentally different from 20 fabric treatment processes which occur in the fabric or clothes manufacturing industries. Laundry compositions contain, as essential ingredients, fabric washing surfactants or fabric conditioning compounds. It is well known in the art that these compounds can interfere with 25 the solubilisation or deposition of soil release polymers.

The present inventors have discovered that many perfluoroalkyl containing polymers, for example as described in US 4043965, show poor deposition onto fabrics and poor adhesion. 30

The present invention sets out to provide laundry compositions which contain high performance soil release

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polymers which have good deposition and provide oil and water repellency to the fabric being laundered.

The present inventors have discovered that perfluoroalkyl
5 polymers which also contain aromatic moieties deposit well onto fabric even from laundry compositions.

Statement of Invention

10 The present invention provides a laundry composition comprising:

(a) a fabric wash detergent, or fabric softening compound,
and

15

(b) a polymeric material obtained by copolymerising an ethylenically unsaturated perfluoroalkyl monomer and, optionally, other ethylenically unsaturated monomers, characterized in that polymeric material comprises aromatic
20 moieties.

The present invention further provides a method of treating fabric, the treatment being carried out as part of the wash step of a laundry operation or the rinse step of a laundry
25 operation, the method comprising treating fabric with polymeric material obtained by polymerising an ethylenically unsaturated perfluoroalkyl monomer and, optionally, other ethylenically unsaturated monomers, wherein the polymeric material comprises aromatic moieties.

30

Detailed Description of the Invention

Polymeric Material

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The polymeric material used in the present invention is obtained by polymerising the monomers defined above. Methods of polymerisation will be discussed further below.

5

Ethylenically Unsaturated Perfluoroalkyl Monomer

Any suitable ethylenically unsaturated perfluoroalkyl monomer may be used.

10

Preferably, the perfluoroalkyl moiety of the monomer is a group R_f according to the general formula (I):

15



20

where m = an integer in the range 3-12, preferably 6-12, and X is a halogen atom, wherein at least 50% of the halogen atoms X are fluorine atoms and the remainder are chlorine or bromine atoms.

The perfluoroalkyl group R_f is preferably of general formula C_qF_{2q+1} or $C_qF_{2q}Cl-$, wherein q is an integer in the range 3-12. It is preferred that q is in the range 6-12, most preferably 8-10.

The ethylenically unsaturated perfluoroalkyl monomer is suitably of general formula (II):

30



- 5 -

wherein A is a divalent linking group, n is 1 or 0, R_f is a perfluoroalkyl moiety as defined above, and Y is an ethylenically unsaturated residue.

- 5 The divalent linking group A is preferably selected from C₁-C₁₈ (optionally substituted) alkenyl, 1,4 phenyl, substituted 1,4 phenyl, C₁-C₁₈ alkenyl chains interrupted by -CO-, -COO-, -OCO-, -NH-, (1,4) phenyl or any other suitable linking group or any combination of such linking groups. Particularly preferred linking groups are alkenyl groups of general formula (III):



- 15 where p is in the range 2-18, more preferably 2-12, and n = 1 or 0

Any suitable ethylenically unsaturated residue X may be used. It is suitably according to general formula IV:

20



- wherein Z is a hydrogen atom, an alkyl group, preferably having 1 to 4 carbon atoms, or a hydroxy alkyl group, preferably having 1 to 4 carbon atoms, B is -COO-, -OCO-, =C=O, or -CONH- and r= 1 or 0.

- Suitably, the ethylenically unsaturated residue is vinyl, substituted vinyl, acrylate, methacrylate, acrylonitrile or the like.

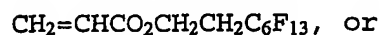
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It is particularly preferred that the ethylenically unsaturated perfluoroalkyl monomer is selected from the group consisting of:

5 1H, 1H, 2H, 2H-perfluorodecacrylate



1H, 1H, 2H, 2H perfluoro octyl acrylate



10



Aromatic Moiety

15 The aromatic moiety may be included in the polymeric material in any suitable manner.

In a first preferred embodiment, the aromatic moiety is introduced by copolymerising the perfluoroalkyl monomer
20 with an ethylenically unsaturated monomer comprising at least one aromatic group.

The ethylenically unsaturated monomer comprising at least one aromatic group is any suitable monomer. Preferably,
25 however, it is selected from aromatic esters of unsaturated compounds, for example benzyl or phenyl ethyl acrylate, benzyl or phenyl ethyl methacrylate, or alkenyl substituted phenyl, for example styrene, alpha-methyl styrene, paramethyl styrene, 3,4-dimethyl styrene, m-ethyl styrene,
30 2,5-diethyl styrene and mixtures thereof.

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In an alternative embodiment, the aromatic group is introduced as a phenylene group in the divalent linking group A, as noted above.

- 5 When the aromatic group is present in the divalent linking group A, the ethylenically unsaturated monomer comprising at least one aromatic group is not necessary, but is still preferred.

10 Optional Ethylenically Unsaturated Co-monomers

- Any suitable ethylenically unsaturated co-monomers may be used. Preferably, the optional ethylenically unsaturated co-monomer is selected from the group consisting of
- 15 ethylene and carboxy, chloro, fluoro, amido and cyano derivatives of ethylene such as vinyl chloride, vinylidene chloride, vinyl fluoride, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, N, N-dimethyl acrylamide, tetrafluoroethylene, hexafluoropropylene, acrylic acid,
- 20 methacrylic acid, acrylate, methacrylate monomers, and mixtures thereof. Particularly preferred are esters of (meth)acrylic acid with alkyl, hydroxyalkyl, alkenyl, hydroxyalkenyl or substituted alkyl with 1-18 carbon atoms, such as n-propylmethacrylate, 2-
- 25 methylcyclohexylmethacrylate, methyl methacrylate, tertiary butyl methacrylate, n-butyl methacrylate, methylacrylate, ethylacrylate, propylacrylate, butylacrylate, 3-methyl pentylacrylate, octylacrylate, tetra-decylacrylate, secondary butylacrylate, 2-ethylhexylacrylate, 2-methoxy
- 30 ethylacrylate, phenylacrylate. Also suitable are nitrogen containing vinyl monomers such as vinylpyridine, N-vinyl amides, N-vinyl succinimide, vinyl pyrrolidone, N-vinyl carbozol, vinyl esters of substituted acids for example

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vinyl methoxyacetate, vinyl trimethylacetate, vinyl isobutyrate, isopropenyl butyrate, vinyl lactate, vinyl caprylate, vinyl myristate, vinyl oleate, vinyl linoleate and vinyl benzoate, mixtures thereof.

5

Particularly preferred are alkyl esters of (meth) acrylic acid.

It is preferred that the polymers of the present invention are amphiphilic. This provides the polymers with valuable surface activity. In order to be amphiphilic, they have to have a hydrophobic moiety and a hydrophilic moiety. The hydrophobic moiety can be provided by the perfluoroalkyl moiety or by hydrophobic ethylenically unsaturated monomers such as alkyl esters of (meth) acrylic acid, particularly long chain (C_8 - C_{18}) alkyl esters of (meth) acrylic acid, for example dodecylacrylate. The hydrophilic moiety is suitably provided by ethylenically unsaturated acidic monomers. Suitable ethylenically unsaturated acidic monomers are selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid, crotonic acid, cinnamic acid, maleic acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, fumaric acid and mixtures thereof.

25

The ethylenically unsaturated acidic monomers may be used in acidic or neutralised form. They may be neutralised with alkalimetal, for example sodium or potassium as counterion.

30

Acrylic acid is particularly preferred.

The acidic ethylenically unsaturated monomer may also provide water solubility to the polymeric material.

Mixing Ratios

5

Any suitable ratios of starting materials may be used. Suitably, the ratios of starting materials are balanced to achieve the physical properties of the polymeric material discussed below.

10

In particular, the quantity of the ethylenically unsaturated perfluoroalkyl containing monomer should be high enough to obtain a good soil release effect when deposited onto fabric. However, there is an upper limit of the quantity of perfluoroalkyl ethylenically unsaturated monomer which reflects the need to ensure that the polymer can be formulated into a stable laundry composition and to ensure that the polymer can be successfully deposited onto fabric and adhered to it.

20

The aromatic moiety is required to assist deposition onto polyester fabric.

Optional other ethylenically unsaturated monomers can be included to provide other suitable properties, for example water solubility.

Suitably, the content of ethylenically unsaturated perfluoroalkyl monomer is in the range 1% by weight - 20% by weight, more preferably 5-15% by weight, most preferably around 5-12% by weight. It is surprising that an acceptable soil release benefit can be obtained with such quantities of ethylenically unsaturated perfluoroalkyl

30

- 10 -

monomer. Prior art compositions relating to non-laundry fabric treatment compositions typically comprise greater than 15% by weight of such monomer.

5 Where the aromatic moiety is incorporated by being part of the ethylenically unsaturated perfluoroalkyl containing monomer, preferably at least 50% by weight of such perfluoroalkyl containing monomer also contains aromatic
10 moieties, more preferably at least 60% by weight. In the embodiment where the aromatic moiety is incorporated by a separate ethylenically unsaturated aromatic monomer, the quantity of ethylenically unsaturated aromatic monomer need not be very high. The quantity can be in the range 3-15% by weight, preferably 5-10% by weight.

15

It is particularly preferred if the polymeric composition contains a large quantity of an ethylenically unsaturated acidic monomer such as acrylic acid. Preferably, the quantity of ethylenically unsaturated acidic monomer is in
20 excess of 50% by weight, more preferably greater than 60% by weight and preferably less than 95% by weight, more preferably less than 90% by weight.

Polymers which are particularly preferred for use in the
25 present invention comprise copolymers comprising:

5-15% by weight of ethylenically unsaturated perfluoroalkyl monomer, 5-10% by weight of ethylenically unsaturated aromatic monomer, 60-90% by
30 weight of ethylenically unsaturated acidic monomer and 0-20% by weight of other copolymerisable ethylenically unsaturated monomers.

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In the above discussion of mixing ratios, all percentages by weight are based upon the total weight of the polymeric material.

5 Physical Properties

The polymers used in the present invention suitably have a number average molecular weight in the range 10,000 to 500,000.

10

The polymers are suitably in the form of solids or viscous liquids.

15 The polymers are suitably soluble in water. Suitably, solubility is in the range 0.2-0.5wt% at 25°C and pH 9.

The polymers used in the present invention have a combined soil release and anti-redeposition benefit.

20 Polymerisation Conditions

Any suitable polymerisation conditions can be used, as is known to the person skilled in the art. For example, the copolymers may be block, graft or random copolymers. They
25 may be produced by solution, emulsion or other polymerisation techniques.

According to a particularly preferred embodiment, the present invention uses polymers manufactured by solution
30 polymerisation in organic solvent.

A homogeneous mixture of the starting monomers is prepared in the organic solvent. Thereafter, polymerisation is

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carried out, in a manner known to the person skilled in the art. Polymerisation conditions can be determined by the person skilled in the art. A suitable radical initiator can be used to induce polymerisation.

5

Any suitable organic solvent can be used, according to the knowledge of the person skilled in the art. For example, petroleum ether or dioxane can be used.

10 Laundry Compositions

The present invention may comprise industrial or domestic fabric wash compositions, fabric conditioning compositions and compositions for both washing and conditioning fabrics
15 (so-called through the wash conditioner compositions).

The perfluoroalkyl containing polymer is suitably present in the laundry fabric compositions of the present invention at levels in excess of 0.5% by weight, preferably greater
20 than 1.0% by weight. They are preferably present at levels less than 10% by weight and preferably less than 5% by weight.

Fabric Wash Compositions

25

Fabric wash compositions according to the present invention may be in any suitable form, for example powdered, tableted powders, liquid or solid detergent bars.

30 Fabric wash compositions according to the present invention preferably comprise a fabric wash detergent material selected from non-soap anionic surfactant, nonionic

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surfactants, soap, amphoteric surfactants, zwitterionic surfactants and mixtures thereof.

Suitable anionic surfactants are well known to the person skilled in the art and include alkyl benzene sulphonate, primary and secondary alkyl sulphates, particularly C₈-C₁₅ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates, dialkyl sulphosuccinates; ether carboxylates; isethionates; sarcosinates; fatty acid ester sulphonates and mixtures thereof. The sodium salts are generally preferred.

Nonionic surfactants are also well known to the person skilled in the art and include primary and secondary alcohol ethoxylates, especially C₈-C₂₀ aliphatic alcohol ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkyl polyglycosides, glycerol monoethers and polyhydroxy amides (glucamide). Mixtures of nonionic surfactant may be used.

Detergent compositions suitable for use in domestic or industrial automatic fabric washing machines generally contain anionic non-soap surfactant or nonionic surfactant, or combinations of the two in suitable ratio, as will be known to the person skilled in the art, optionally together with soap.

Many suitable detergent-active compounds are available and fully described in the literature, for example in Surface-

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Active Agents and Detergents , Volumes I and II, by
Schwartz, Perry & Berch.

Anionic surfactant is suitably present at a level of from 5
5 wt% to 50 wt%, preferably 10 wt%-40 wt% based on the fabric
treatment composition. Nonionic surfactant is suitably
present at a level of 1-20 wt%, preferably 5-15 wt%.

The total amount of surfactant present will depend upon the
10 intended end use and may be as high as 60 wt% for example
in a composition for washing fabrics by hand. In
compositions for machine washing of fabric, an amount of
from 5 to 40 wt% is generally appropriate.

15 Detergency Builder

The fabric wash compositions of the invention will
generally also contain one or more detergency builders.
The total amount of detergency builder in the compositions
20 will suitably range from 5 to 80 wt%, preferably from 10 to
60 wt%.

Inorganic builders that may be present include sodium
carbonate, if desired in combination with a crystallisation
25 seed for calcium carbonate, as disclosed in GB 1 437 950
(Unilever); crystalline and amorphous aluminosilicates,
for example, zeolites as disclosed in GB 1 473 202 (Henkel)
and mixed crystalline/amorphous aluminosilicates as
disclosed in GB 1 470 250 (Procter & Gamble); and layered
30 silicates as disclosed in EP 164 514B (Hoechst). Inorganic
phosphate builders, for example, sodium orthophosphate,
pyrophosphate and tripolyphosphate are also suitable for
use with this invention.

- 15 -

The fabric wash detergent compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may
5 generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general
10 formula:



These materials contain some bound water and are required
15 to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO₂ units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as
20 amply described in the literature.

Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium
25 aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

The zeolite may be the commercially available zeolite 4A
30 now widely used in laundry detergent powders. The zeolite builder incorporated in the compositions of the invention may be maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite

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MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates,; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

Especially preferred organic builders are citrates, suitable used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.

Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

30

Bleach Components

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Laundry compositions according to the invention may also suitably contain a peroxy bleach system for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution.

5

Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic
10 persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture.

15 Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

The compositions may further comprise a photobleach system
20 as described, for example, in EP-A-0035470.

Fabric Softening Composition

The fabric treatment composition of the present invention
25 may be a fabric conditioning composition or it may comprise fabric conditioner.

Fabric Softening Compound

30 The fabric softening compound is preferably a cationic nonionic or anionic fabric softening compound.

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The fabric softening compound may be a quaternary ammonium material comprising a polar head group and one or two alkyl or alkenyl chains. The fabric softening compound may also be a nonionic fabric softening compound such as a fabric softening oil, a fabric softening silicone composition or a fabric softening ester composition such as sugar esters.

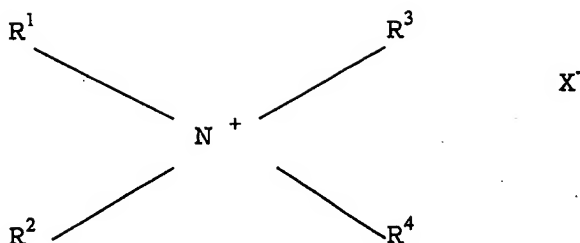
Particularly preferably, the fabric softening compound has two long chain alkyl or alkenyl chains with an average chain length greater than C_{14} , more preferably each chain has an average chain length greater than C_{14} , more preferably at least 50% of each long chain alkyl or alkenyl group has a chain length of C_{18} .

It is preferred if the long chain alkyl or alkenyl groups of the fabric softening compound are predominantly linear.

It is highly preferred if the fabric softening compounds are substantially water-insoluble. Substantially insoluble fabric softening compounds in the context of this invention are defined as fabric softening compounds having a solubility less than 1×10^{-3} wt% in demineralised water at 20°C , preferably the fabric softening compounds have a solubility less than 1×10^{-4} , most preferably the fabric softening compounds have a solubility at 20°C in demineralised water from 1×10^{-3} to 1×10^{-6} .

Well known species of substantially water-insoluble quaternary ammonium compounds having the formula:

- 19 -



wherein R^1 and R^2 represent hydrocarbyl groups having from 12 to 24 carbon atoms; R^3 and R^4 represent hydrocarbyl groups containing 1 to 4 carbon atoms; and X is an anion, preferably selected from halide, methyl sulphate and ethyl sulphate groups are preferred.

Representative examples of these quaternary softeners include di(tallow alkyl) dimethyl ammonium methyl sulphate; dihexadecyl dimethyl ammonium chloride; di(hydrogenated tallow alkyl) dimethyl ammonium chloride; dioctadecyl dimethyl ammonium chloride; di(hydrogenated tallow alkyl) dimethyl ammonium methyl sulphate; dihexadecyl diethyl ammonium chloride; di(coconut alkyl) dimethyl ammonium chloride, ditallow alkyl dimethyl ammonium chloride and di(hydrogenated tallow alkyl) dimethyl ammonium chloride (Arquad 2HT Trade Mark).

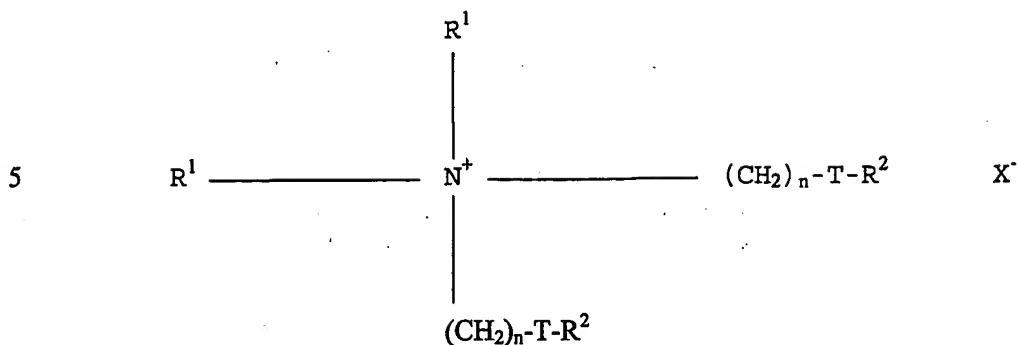
Other preferred softeners contain esters or amide links, for example those available under the trade names Accosoft 580, Varisoft 222, and Stepantex.

Particularly preferred fabric softening compounds are water-insoluble quaternary ammonium materials which comprise a compound having two C_{12-18} alkyl or alkenyl groups connected to the molecule via at least one ester

- 20 -

link. It is more preferred if the quaternary ammonium material has two ester links present. The preferred ester-linked quaternary ammonium material for use in the invention can be represented by the formula:

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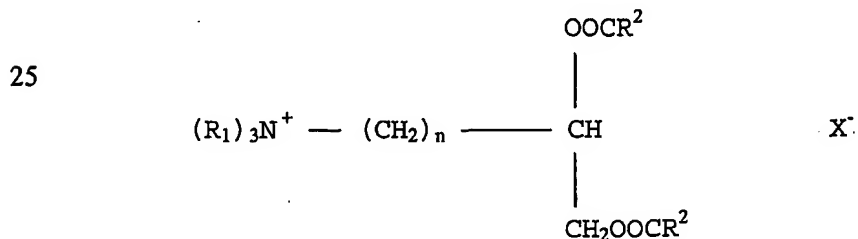


10 wherein each R^1 group is independently selected from C_{1-4} alkyl, hydroxyalkyl or C_{2-4} alkenyl groups; and wherein each R^2 group is independently selected from C_{8-28} alkyl or alkenyl groups;

15 T is $\begin{array}{c} O \\ || \\ -C-O- \end{array}$ or $\begin{array}{c} O \\ || \\ -O-C- \end{array}$; X^- is any suitable anion and n is an integer from 0-5. Particularly preferred is di(ethyl ester) dimethyl ammonium chloride (DEEDMAC).

20

A second preferred type of quaternary ammonium material can be represented by the formula:



30 wherein R_1 , n , X^- and R_2 are as defined above.

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It is advantageous for environmental reasons if the quaternary ammonium material is biologically degradable.

Preferred materials of this class such as 1,2 bis[hardened
5 tallowyloxy]-3-trimethylammonium propane chloride and
their methods of preparation are, for example, described in
US 4 137 180 (Lever Brothers). Preferably these materials
comprise small amounts of the corresponding monoester as
described in US 4 137 180 for example 1-hardened
10 tallowyloxy-2-hydroxy trimethylammonium propane chloride.

The fabric softening agent may also be a polyol ester quat
(PEQ) as described in EP 0 638 639 (Akzo).

15 The present invention may be in the form of a dilute or
concentrated aqueous solution or suspension, for example as
described in WO 97/15651, WO 95/27769. Alternatively, the
fabric softening composition may be in the form of a powder
for use in the rinse cycle of an automatic washing machine.
20 Alternatively, the fabric softening composition may be in
the form of a sheet comprising fabric conditioning
compositions for use in a tumble dryer, for example as
disclosed in WO 95/27777.

25 Fabric wash detergent compositions according to the present
invention may further include through the wash softening
material, such as cationic fabric softener.

Other Ingredients

30

The laundry compositions of the invention can also contain
one or more optional ingredients, selected from pH
buffering agents, perfume carriers, fluorescers, colorants,

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hydrotropes, antifoaming agents, antiredeposition agents, enzymes, optical brightening agents, opacifiers, anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, germicides, fungicides, anti-corrosion agents, drape imparting agents, antistatic agents and ironing aids.

Examples

The present invention will be further described by way of example only.

Test Methods

Testing Adhesion of Polymers to Fabric

A 0.2 wt% aqueous solution of polymer was prepared. 3.5cm x 3.5cm test sheets of fabric were taken. The fabrics were desized before use by boiling in 1 molar sodium carbonate for 30 minutes. After washing to a neutral pH, the fabric is boiled continuously for a further 30 minutes and oven dried at 50°C in an oven. The desized fabrics were soaked in the aqueous solution at 25°C. After soaking for 30 minutes, the cloths were removed and rinsed with distilled water. The resulting cloths were oven dried at 50°C for 1 hour. The increase in dry weight was measured. Polyester and cotton test sheets were tested separately.

Soil Release

Polyester fabric was treated as set out above. Soil release was tested by placing 17 x 0.1.ml drops of oil comprising 15 mg sudan IV oil dissolved in 100 ml of sesame oil on the approximate centre of each test specimen using a

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laboratory pipette. Oil was allowed to wick for 24 hours. The test cloths were then washed at 25°C for 30 minutes of 375 revolutions per minute in water only. The reflectance data at 520 nm were measured for fabric after oil staining and after washing. Comparison with reflectance data after washing shows the extent of soil release of the polymer. Reflection is measured using a colour-eye spectrometer at 520 nm.

10 Soil Deposition

The ability of the polymers to prevent soil redeposition was assessed as follows. An untreated polyester or cotton cloth was washed in 100 ml of water comprising 0.1% by weight carbon black and 0.25 Wt% of a detergent composition containing the polymer at 25°C for 1.5 hours at 375 rs/m, rinsed and oven dried at 50°C.

The detergent compositions were as follows:

20 NaCl - 33% by weight

 Sodium carbonate - 25% by weight

 Anionic surfactant (LAS) - 20% by weight

25

 Sodium tripolyphosphate builder - 22% by weight

 Polymeric material - 4% by weight.

30 Rinsing was carried out for 5 minutes. Reflectance was assessed at 520 nm using the Macbeth (trade mark) Colour Eye Spectrometer.

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Reference Example 1 - Preparation of Polymer

A homogeneous mixture of monomeric starting materials in 1,4 dioxane was prepared.

5

The monomer mixture comprised the following:

1H,1H,2H,2H-heptadecafluorodecylacrylate (T-AN) - 2.6 mole %.

10

Acrylic acid - 92.3 mole %.

Styrene - 5.1 mole %.

15 2 -azobisiso-butyronitrile (AIBN) radical initiator was added.

Monomer concentration in the solvent was 10 wt% approximately. The solvent comprised 1 wt% AIBN based upon
20 the total monomer content.

Polymerisation was carried out at 80°C for 6 hours with continuous stirring. Before polymerisation, the components were degassed by the application of the freeze-thaw
25 technique.

The polymer product was isolated by triturating in petroleum ether. The isolated product was dried under vacuum at 60°C to give a final product. Yield was approx
30 90wt%.

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The experiment was repeated with various comparative monomer mixtures. The compositions of the monomer mixtures are set out in Table 1 below.

5 The polymers were all solid precipitates.

The polymer products were analysed using infrared spectroscopy (using a Shimadzu IR-440 or Digilab FTS-20E Spectrometer [trade mark]). ^1H spectra were recorded with
 10 a Bruker (trade mark) AM-300 Spectrometer. ^{19}F NMR spectra were then recorded using the same spectrometer. C and H elements were assessed using a Carlo-Erba 1106 Elemental Analyser. The fluorine content could also be analysed
 15 techniques described were used to assess the quantities of monomers in the resulting polymers. The results are shown in Table 1.

In Table 1, T-AN and AA have the meaning set out above, or
 20 their corresponding repeat units. The following species are found to be present:

- $(\text{CH}_2\text{CHR})_m - (\text{CH}_2\text{CHX})_n -$
 - $(\text{CH}_2\text{CHR})_m - (\text{CH}_2\text{CHX})_n - (\text{CH}_2\text{CHY})_t -$
 25 - $(\text{CH}_2\text{CHR})_m - (\text{CH}_2\text{CHX})_n - (\text{CH}_2\text{CHZ})_t -$
 - $(\text{CH}_2\text{CHR})_m - (\text{CH}_2\text{CHX})_n - (\text{CH}_2\text{CHZ})_t -$

where:

m, n and t are integers,

30 X is $-\text{COOH}$

Y is $-\text{CO}_2\text{C}_{12}\text{H}_{25}$,

Z is $-\text{CO}(\text{OCH}_2\text{CH}_2)_p\text{OCH}_3$, where $p=6.9$,

P is C_6H_5- ,

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and R is $-\text{CO}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17}$

Table 1

polymer	feed ratio (wt%)			Polymer compn (wt%)			
	T-AN	AA	other	$-\text{CH}_2\text{CHR}$	$-\text{CH}_2\text{CHX}$	other	MWT
a	4.5	95.5	-	2.1	97.9	-	4.89
b	2.0	98.0	-	3.2	96.8	-	-
c	2.8	94.4	CH_2CHY 2.8	2.0	95.2	CH_2CHY 2.8	2.58
d	2.8	94.4	CH_2CHZ 2.8	2.1	94.1	CH_2CHZ 3.8	2.91
e	2.6	92.3	CH_2CHP 5.1	1.7	92.7	CH_2CHP 5.6	

5

All percentages are mole %.

Absorption of polymers e (according to the present invention) and a (comparative) were tested as set out above.

10 Also tested was Gerol (trade mark), a commercially available soil release polymer. Table 2 below sets out the polymers used, pH and resulting deposition with polymers according to the present invention (polymer e), and fluoroalkyl/acrylic acid polymer (polymer a) and Gerol as
15 comparisons.

Table 2

Adsorption Measurement of Copolymers

Example	1	2	3	4	5
Polymers	e	e	a	a	GEROL
pH	4	9	9	4	
Fabric wt. (mg) After Treatment	358.70	321.74	207.39	290.95	361.15
Fabric wt. (Mg) After Treatment	359.06	322.09	207.43	291.14	361.62
Deposition (mg)	0.36	0.35	0.04	0.19	0.47
wt% Increase	0.1	0.11	0.017	0.067	0.13

- 5 It can be seen that polymer e according to the invention gives a much improved deposition compared to the fluoroalkyl/acrylic acid polymer and a comparable deposition to the product Gerol (trade mark).
- 10 Soil release properties were assessed according to the methods set out above. The soil release properties obtainable using polymer according to the present invention (polymer e) was compared with soil release obtained with an acrylic acid/perfluoroalkyl copolymer (polymer a) and
- 15 commercially available Gerol (trade mark) copolymer. The results are set out in Table 3 below.

Table 3

Reflectance data at 520 nm wavelength	
Polymer	ΔR
e	9.566
a	4.394
Gerol	5.648
None	0.196

- 5 It can be seen that very high levels of reflectance can be obtained with polymers according to the present invention, exceeding even the commercially available product Gerol.

10 The effect on soil deposition was then assessed by the methods set out above. The antiredeposition effect of polymers used according to the present invention was compared with that of the polymer Gerol (trade mark) and of a composition containing no anti-redeposition polymer.

- 15 The composition comprising no anti-reposition polymer comprised 33% by weight sodium chloride instead of 29% by weight sodium chloride, to make up the weight. A further comparison was conducted by washing with water only. The results are shown in Table 4.

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Table 4

Reflectance data at 520 nm wavelength	
Polymer	ΔR
Gerol	6.116
e	17.003
none	39.453
water only	47.126

- 5 It can be seen that the decrease in reflectivity (which is
a measure of the tendency of the carbon black to deposit
onto the fabric during washing) is significantly less for
polymers used according to the present invention than for
compositions containing no polymer. The decrease in
10 reflectance is not as good as for the commercial product
Gerol, but it is still acceptable.

The invention has been described above by way of example
only and modifications can be made within the invention.

CLAIMS:

1. A laundry composition comprising:

- 5 (a) a fabric wash detergent or a fabric softening compound, and
- (b) polymeric material obtained by polymerising an ethylenically unsaturated perfluoroalkyl monomer and,
10 optionally, other ethylenically unsaturated monomers characterized in that polymeric material comprises aromatic moieties.

2. A method of treating fabrics, the treatment being
15 carried out as part of the wash step of a laundry operation or the rinse step of the laundry operation, the method comprising treating the fabric with polymeric material obtained by polymerising an ethylenically unsaturated perfluoroalkyl monomer and, optionally, other ethylenically
20 unsaturated monomers characterized in that polymeric material comprises aromatic moieties.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/06377

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/37 D06M15/277

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 954 545 A (BAILEY FAY W) 4 September 1990 (1990-09-04) claim 1	1
X	EP 0 909 802 A (DAIKIN IND LTD) 21 April 1999 (1999-04-21) paragraphs '0001!'-'0003!', '0006!', '0007!'; claim 1	1,2
X	US 5 753 569 A (MICHELS GISBERT ET AL) 19 May 1998 (1998-05-19) cited in the application column 1, line 9-12 column 1, line 65 -column 2, line 8; claim 1	1,2

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Z document member of the same patent family

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Pentek, E

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 695 488 A (HISAMOTO IWAO ET AL) 22 September 1987 (1987-09-22) cited in the application column 1, line 6 -column 2, line 64; claims 1,11	1,2
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A	US 6 075 003 A (PETRI CARLOS ET AL) 13 June 2000 (2000-06-13) claim 1	1,2

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Information on patent family members

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